

5 **USE OF AN OXIDIZING SYSTEM COMPRISING A MACROCYCLIC
METAL COMPLEX AND AN OXIDIZING AGENT FOR REMOVING
EXCESS, UNFIXED DYE FROM DYED, TEXTILE MATERIALS**

BACKGROUND OF THE INVENTION

Field of the Invention: The present invention relates to the use of an
oxidizing system, comprising a macrocyclic metal complex and an
10 oxidizing agent for removing excess, unfixed dye from dyed textile
materials, and the resulting textiles.

Brief Description of the Prior Art: US-A-6,099,586 and WO-A-02/16330
disclose specific macrocyclic metal complexes useful as bleach activators.
Combined with a peroxide source, preferably hydrogen peroxide, these
15 bleach activators make it possible to carry out oxidation reactions. Such
oxidation reactions are carried out for example in paper bleaching, for
decolorizing coloured wastewaters or in the desulphurization of motor
fuels. Also described is the use in household laundry detergents for
respectively removing and decolorizing soil on the laundry and in the wash
20 liquor. In all these applications, the use of the specific macrocyclic metal
complexes leads to an improvement in the results compared with the sole
treatment with a peroxide source.

There is a fundamental problem in the textile industry with removing
excess, unfixed dye from textiles after dyeing or printing. The colouring of
25 textile material, i.e., printing or dyeing, will hereinafter be circumscribed
using the term "dyeing".

To remove unfixed dye, the dyer has to carry out a very time- and cost-
intensive washing operation after the actual dyeing. This is the only way of
achieving consumer quality with regard to washing, rubbing and staining
30 fastness. One approach to shortening the washing operation after the
dyeing of textile material was demonstrated in WO-A 92/18687 and EP-A-

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01 045 934 with reference to the use of enzymatic-based additive systems.

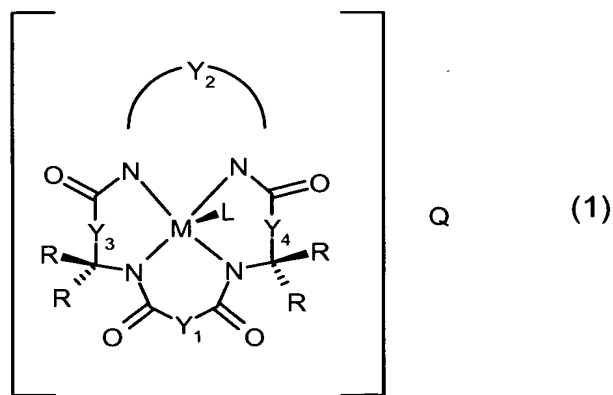
SUMMARY OF THE INVENTION

It has now been found that, surprisingly, the use of an oxidizing system comprising a macrocyclic metal complex and an oxidizing agent provides excellent decolorization of excess, unfixed dye from dyed textile materials.

This process advantageously provides highly selective removal of excess, unfixed dye from the dyed textile, without the dyed textile itself being decolorized.

The invention accordingly provides for the use of an oxidizing system comprising the two components

1) a macrocyclic metal complex of the general formula (1)



where

Y₁, Y₃ and Y₄ are each independently a single bond or a bridge member which contains 1, 2 or 3 carbon atoms in the bridge,

Y₂ is a bridge member having at least 1 carbon atom in the bridge,

R is independently in each occurrence hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy, phenoxy, CH_2CF_3 or CF_3 or two R radicals which are bound to the same carbon atom combine to form a substituted or unsubstituted benzene, cycloalkyl or cycloalkenyl ring, the carbon atom to which the two R radicals are bound being part of the benzene, cycloalkyl or cycloalkenyl ring,

M is a transition metal in the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 and 11 of the periodic table,

Q is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis, and

L is a further ligand

and

2) an oxidizing agent

for removing excess, unfixed dye from dyed textile materials.

DETAILED DESCRIPTION OF THE INVENTION

The invention is described more fully hereunder with particular reference but without limitation to its preferred embodiments. Preferably, in the macrocyclic metal complex of the general formula (1)

Y_1 , Y_3 and Y_4 are each independently a $(-\text{CH}_2-)_x$ group, where x is 1, 2 or 3 and one or more hydrogen atoms in the $(-\text{CH}_2-)_x$ group may be substituted by an R^i radical, R^i being alkyl, cycloalkyl,

5 cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy, or two R^i radicals which are bound to two adjacent carbon atoms of the $(-CH_2-)_x$ group combining to form a benzene, cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms, preferably N, O or S.

Preferably, in the macrocyclic metal complex of the general formula (1)

10 Y_2 is a bridge member having 1, 2 or 3 carbon atoms in the bridge, preferably a $(-CH_2-)_y$ group, where y is 1 or 2 and one or more hydrogen atoms in the $(-CH_2-)_y$ group may be substituted by an R^{ii} radical, R^{ii} being alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy, or two R^{ii} radicals which are bound to two adjacent carbon atoms of the $(-CH_2-)_y$ group combining to form an optionally substituted benzene, cycloalkyl or cycloalkenyl ring
15 which may contain one or more hetero atoms, preferably N, O or S, preferably a benzene ring which may be substituted by electron-donating or electron-withdrawing radicals.

In the macrocyclic metal complex of the general formula (1)

20 the R radicals are each independently hydrogen, C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, C_4 - C_{12} -cycloalkenyl, C_2 - C_8 -alkenyl, C_6 - C_{14} -aryl, C_2 - C_{12} -alkynyl, C_1 - C_{12} -alkylaryl, halogen, alkoxy, phenoxy, CH_2CF_3 or CF_3 or two R radicals which are bound to the same carbon atom combined to form a substituted or unsubstituted benzene, C_3 - C_8 -cycloalkyl or C_4 - C_{12} -
25 cycloalkenyl ring, the carbon atom to which the two R radicals are bound being part of the benzene, cycloalkyl or cycloalkenyl ring.

The metal M in the macrocyclic metal complex of the general formula (1) is a transition metal having the oxidation states I, II, III, IV, V or VI or from groups 6, 7, 8, 9, 10 or 11 of the periodic table. Preferably, the metal M represents Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and/or Pt.

- 5 Mixtures of metals of the aforementioned oxidation states or from the aforementioned groups of the periodic table are likewise possible.

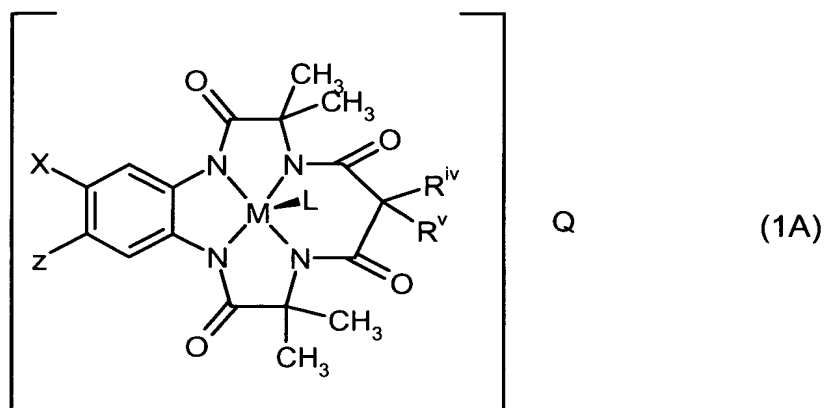
- Q in the macrocyclic metal complex of the general formula (1) is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis. The metal-ligand complex is customarily
10 negative, preferably -1 . Consequently, the counterion generally has a positive charge, given a preferred negative charge of -1 , is accordingly $+1$.

- Suitably, Q is an alkali metal counterion, preferably potassium, lithium or sodium, $\text{NR}^{\text{iii}}_4^+$ or $\text{PR}^{\text{iii}}_4^+$, where every R^{iii} is independently hydrogen, alkyl, aryl, alkylaryl, alkenyl or joins to form a cycloalkyl, cycloalkenyl or aryl ring
15 which optionally contains one or more hetero atoms, preferably oxygen, sulphur or nitrogen.

L is any further ligand which can attach to M. Preferably, L is a labile ligand, especially H_2O , Cl or CN.

- The aforementioned preferred and particularly preferred meanings for Y_1 -
20 Y_4 , R, R^{i} , R^{ii} , R^{iii} , Q and L may be combined in any desired manner.

In a preferred embodiment, the invention comprises the use of an oxidizing system which comprises a macrocyclic metal complex which has the general formula (1A)



where

- X and Z are each independently hydrogen, electron-donating or electron-withdrawing groups,
- 5 R^{iv} and R^v may each independently be hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, alkylaryl, halogen, alkoxy or phenoxy radicals or combine to form a cycloalkyl or cycloalkenyl ring which may contain one or more hetero atoms, preferably oxygen, sulphur or nitrogen,
- 10 M is a transition metal of the oxidation states I, II, III, IV, V or VI or is selected from groups 6, 7, 8, 9, 10 or 11 of the periodic table,
- Q is a counter ion which balances the charge of the macrocyclic metal complex on a stoichiometric basis, and
- 15 L is a further ligand.

In the macrocyclic metal complex of the formula (1A), X and Z may each be independently hydrogen or electron-donating or electron-withdrawing radicals. Electron-donating or electron-withdrawing radicals change the

electron density of the metal-ligand complex and thus influence its reactivity.

Suitable electron-withdrawing radicals are for example halogens, preferably chlorine, bromine or iodine, more preferably chlorine, SO_3^- ,
5 OSO_3^- , $\text{OSO}_3\text{R}^{\text{vi}}$ (where R^{vi} is hydrogen, alkyl, aryl or alkylaryl) or NO_2^- .

Suitable electron-donating radicals are for example C_1 - C_8 -alkoxy, preferably methoxy, ethoxy, propoxy and butoxy, C_1 - C_8 -alkyl, preferably methyl, ethyl, propyl, n-butyl and tert-butyl, and hydrogen.

In the macrocyclic metal complex of the formula (1A), R^{iv} and R^{v} are each
10 independently hydrogen, alkyl, cycloalkyl, cycloalkenyl, alkenyl, aryl, alkynyl, halogen, alkoxy or phenoxy radicals. R^{iv} and R^{v} are preferably each independently alkyl, particularly preferably C_1 - C_5 -alkyl. More preferably R^{iv} and R^{v} are both identically methyl or ethyl. Even more preferably, R^{iv} and R^{v} combine to form a cycloalkyl ring, especially a
15 cyclopentyl or cyclohexyl ring, or a cycloalkenyl ring. This cycloalkyl or cycloalkenyl ring may contain one or more hetero atoms, preferably oxygen, sulphur or nitrogen.

The metal M in the macrocyclic metal complex of the general formula (1a) is a transition metal having the oxidation states I, II, III, IV, V or VI or is
20 selected from groups 6, 7, 8, 9, 10 or 11 of the periodic table. Preferably, the metal M represents Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and/or Pt. Mixtures of metals of the aforementioned oxidation states or from the aforementioned groups of the periodic table are likewise possible.

25 Q in the macrocyclic metal complex of the general formula (1a) is a counterion which balances the charge of the macrocyclic metal complex on a stoichiometric basis. The metal-ligand complex is customarily

negative, preferably -1 . Consequently, the counterion generally has a positive charge, given a preferred negative charge of -1 , is accordingly $+1$.

Suitably, Q is an alkali metal counterion, preferably potassium, lithium or sodium, $\text{NR}^{\text{iii}}_4^+$ or $\text{PR}^{\text{iii}}_4^+$, where every R^{iii} is independently hydrogen, alkyl, aryl, alkylaryl, alkenyl or combines to form a cycloalkyl, cycloalkenyl or aryl ring which optionally contains at least one further atom, as carbon.

In the macrocyclic metal complex of the general formula (1A) L is any further ligand which can attach to M. Preferably, L is a labile ligand, especially H_2O , Cl or CN.

10 The preparation of the macrocyclic metal complexes used in accordance with the invention is described in EP-A-918 840, US-A-6,099,586 and WO-A-02/16330, each of which is hereby explicitly incorporated herein by reference.

The oxidizing agent can be any organic or inorganic oxidizing agent. A peroxy compound is typically used. Suitable peroxy compounds are hydrogen peroxide, hydrogen peroxide adducts, compounds capable of releasing or generating hydrogen peroxide in aqueous solution, organic peroxides, persulphates, perphosphates and persilicates.

Hydrogen peroxide adducts include alkali metal, preferably sodium, lithium or potassium, carbonate peroxyhydrate and also urea peroxide.

Compounds capable of generating hydrogen peroxide in aqueous solution include alkali metal, preferably sodium, potassium or lithium, perborate (as mono- or tetrahydrate). Such perborates are commercially available.

Alternatively, an alcohol oxidase and its appropriate alcohol substrate can be used as peroxide source.

Organic peroxides include benzoyl and cumene hydroperoxides.

Persulphates include peroxymonosulphate and Caro's acid.

Particularly preferred oxidizing agents are hydrogen peroxide and sodium perborate.

The macrocyclic metal complex is used in the oxidizing system in an amount in the range from 0.01 μmol to 1000 μmol . Preference is given to an amount in the range from 0.1 μmol to 100 μmol .

The oxidizing agent is used oxidizing system in an amount in the range of 0.01-1000 mmol. Preference is given to an amount in the range of 0.1-100 ppm.

10 The inventive use is preferably carried out by the dyed textile material being contacted with the oxidizing system in at least one of the post-dyeing rinse steps.

The dyeing can be dyeing with any commercially available dye. Reactive dyes, direct dyes, substantive dyes, acid dyes, metal complex dyes, 15 disperse dyes, vat dyes and sulphur dyes may be mentioned.

The dyeing has preferably been carried out with water-soluble dyes and more preferably with reactive dyes.

Preferably, the dyed textile material is contacted with the oxidizing system in at least one of the post-dyeing rinse steps by at least one of the rinse 20 liquors having the two components of the oxidizing system added to it either individually in any order or else individually and concurrently.

More preferably, the dyed textile material is contacted with the oxidizing system in one of the post-dyeing rinse steps.

The macrocyclic metal complex is typically added in the form of an aqueous solution to which may optionally have been added 0.5-40% by 25 weight, based on the entire solution, of a pH stabilizer and of a water-

soluble or at least partially water-soluble solvent. As suitable water-soluble solvents there may be mentioned ethanol, methanol, isopropanol, ethylene glycol, diethylene glycol, polyethylene glycols, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, diethylene glycol monobutyl ether, acetone, acetonitrile, acetamide, tetrahydrofuran, 5 dioxane, dimethyl sulphoxide, dimethyl formamide, sulpholane or mixtures thereof. Suitable pH stabilizers are phosphate, citrate buffer, carbonate buffer or borate buffer, or mixtures thereof.

When hydrogen peroxide is used as oxidizing agent, it is used in the form 10 of for example commercially available aqueous solutions having an assay of 3-50%.

It may be advantageous to use not only the oxidizing system in the inventive use but also further additives, such as deterative substances, preferably surfactants, sequestrants, defoamers, enzymes, such as 15 amylases, pectinases, proteases, peroxidase, laccases or lipases, water-conditioning agents, such as water softeners, pH stabilizers, such as phosphate, citrate buffer, carbonate buffer or borate buffer, or mixtures thereof, or solvents which are soluble or at least partially soluble in water. Suitable water-soluble solvents are ethanol, methanol, isopropanol, 20 ethylene glycol, diethylene glycol, polyethylene glycols, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, diethylene glycol monobutyl ether, acetone, acetonitrile, acetamide, tetrahydrofuran, dioxane, dimethyl sulphoxide, dimethyl formamide, sulpholane or mixtures thereof.

25 Such additives are used at 0-50% by weight and preferably 0.01-30% by weight, based on the rinse liquor.

The treatment time of the dyed textile material in a rinse step depends on the type and amount of excess dye to be decolorized. Generally, 2-60 minutes are sufficient. If appropriate, a further addition of either any one or

both of the components of the oxidizing system can be advantageous during the treatment.

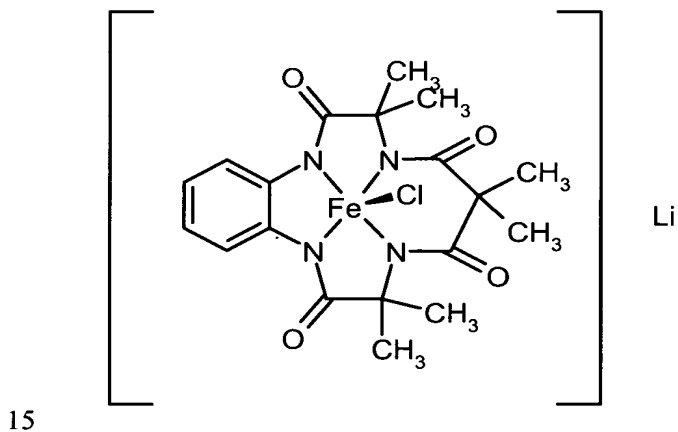
The dyed textile materials may be cotton, filament viscose, staple viscose, lyocell, wool, silk, polyester, polyamide, polyacrylonitrile and elastane or
5 blends thereof. The dyed textile materials are more preferably cotton, filament viscose and lyocell or blends thereof with polyester, polyamide or elastane.

The process for removing excess, unfixed dye is customarily carried out at a temperature of 25-95°C and preferably 40-80°C. Rinse liquor pH is in
10 the range of 4-13, preferably 5-12 and more preferably 7-11.

The invention is further described by the following illustrative but non-limiting examples.

EXAMPLE

The example hereinbelow utilizes a macrocyclic metal complex



which is prepared by the method described in Examples 1-6 of WO-A-02/16330. This compound is hereinbelow referred to as **1b**.

The starting point is a scoured and bleached cotton formed-loop knit which is dyed in a laboratory dyeing machine (a Mathis Spectradye for example) at a liquor ratio of 10:1 using the following recipe:

10 g of cotton are pretreated in a liquor consisting of

- 5 0.4 g/l of RESPUMIT[®] NF
 0.5 g/l of PERSOFTAL[®] L and
 80 g/l of sodium chloride

at 25°C for 10 minutes. The temperature is raised to 50°C, when

8% on weight of fibre of Remazol[®] Deep Black N,

- 10 is added in 3 portions at intervals of 10 minutes. This is followed, after a further interval of 10 minutes by the addition of 2.0 g/l of sodium carbonate in three portions at intervals of 10 minutes. This is followed after a further 10 minutes by the addition of 3.0 g/l of 50% aqueous sodium peroxide solution in three portions at intervals of 10 minutes. This is finally followed
15 by heating to 60°C at 1°C/min and then a 60 minute treatment at 60°C. Immediately following dyeing, the dyed sample is rinsed in a liquor ratio of 10:1 as follows:

- drain the dyeing liquor
- (1st rinse step) addition of fresh water, rinse at 60°C for 10
20 minutes, drain the liquor
- (2nd rinse step) addition of fresh water at 95°C for 10 minutes, drain the liquor
- (3rd rinse step) addition of fresh water together with 1 µmol of compound **1b**, treat at 60°C for 5 minutes, addition of 4.4 mmol
25 of hydrogen peroxide, treat at 60°C for 10 minutes, drain the liquor

- (4th rinse step) addition of fresh water, rinse at 40°C for 10 minutes and drain the liquor

Finally, the sample is centrifuged and dried.

- 5 A comparative test is carried out with the third rinse step being carried out without addition of compound **1b** and without hydrogen peroxide. Otherwise all the steps are carried out in the same way.

The table below shows the colour of the individual rinse liquors (determined as absorbance at 598 nm; the lower the absorbance, the lower the colouredness):

	Inventive process	Comparative test
After:	absorbance at 598 nm	absorbance at 598 nm
2nd rinse step	about 7.6	about 7.6
3rd rinse step	0.5	about 3.2
4th rinse step	0.3	1.2

10

The results clearly show the significantly better decolorization of the rinse liquor in bath 3 in the presence of compound **1b** and hydrogen peroxide and the attendant lower colour of the last rinse liquor for the inventive process.

- 15 The wash-off effect is evaluated by determining the waterfastness of the dyeing in accordance with German standard specification DIN 54006 (waterfastness of dyeings, severe exposure). Cotton is used as adjacent fabric. The evaluation scale goes from 1 to 5, where 5 denotes the best fastness.

	Inventive process	Comparative test
Rating	2	2-3

The inventive process accordingly provides a substantial improvement in waterfastness by half a rating point.

5 The treatment with the inventive oxidizing system has not affected the dyeing on the cotton.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may
10 be limited by the claims.